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(54) Title: BIODEGRADABLE POLYMERIC COMPOSITIONS BASED ON STARCH AND THERMOPLASTIC POLYMERS			
(57) Abstract			
A thermoplastic polymeric composition including starch, at least one synthetic thermoplastic polymer and a plasticiser in which the plasticiser is at least one compound selected from the group consisting of: a) polyols formed by from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms, provided that when the polyol is formed by only one repeating unit it has at least 4 carbon atoms, with the exclusion of sorbitol, b) ethers, thioethers, inorganic and organic esters, acetals and amino-derivatives of polyols formed by from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms with the exclusion of acetic esters of glycerine, triethyl citrate and tributyl citrate, c) polyol reaction products having from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms with chain extenders; d) polyol oxidation products having from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms including at least one aldehydic or carboxylic functional group or mixtures thereof.			

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Biodegradable polymeric compositions based on starch and thermoplastic polymers

The present invention relates to thermoplastic polymeric compositions including starch and synthetic thermoplastic polymers and suitable for producing substantially biodegradable articles having satisfactory physical and mechanical properties by conventional techniques for the processing of thermoplastic materials.

Thermoplastic compositions of the type mentioned above are described in patent applications Nos. EP-A-32802, EP-A-327 505, EP-A-404 723, EP-A-404 727, EP-A-404 728 and EP-A-400532. Typically, these compositions are produced by the mixing of a starch with one or more synthetic thermoplastic polymers by means of a process which can destroy the crystallinity of the starch and create a structure which is interpenetrated or at least partially interpenetrated by the synthetic polymers. These processes may vary significantly in dependence on the chemical, physical and rheological characteristics of the synthetic component and the types of additives present.

Examples of these processes are described in patent applications Nos. EP-A-413798 and EP-A-400532.

The use of pharmaceutically-acceptable plasticising compositions with low molecular weights such as glycerine, acetic esters of glycerine, ethylene glycol, propylene glycol, sorbitol, sodium dioctylsulphosuccinate, triethyl citrate and tributyl citrate, in particular, in such compositions is known.

It has been found that, mainly because of changes in humidity and temperature undergone by articles produced

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by the processing of such plasticised compositions over a period of time, the articles are subject to the sweating (bleeding) and/or evaporation of the plasticiser which sometimes forms an oily film and sometimes crystalline dust on the surface of the article, thus limiting the article both from an aesthetic point of view and from the point of view of its handling.

The object of the present invention is to prevent the bleeding which takes place when known and conventional plasticisers are used.

For this purpose, a subject of the present invention is a thermoplastic polymeric composition including starch, at least one synthetic thermoplastic polymer and a plasticiser, and in which the starch and the polymer form a structure in which they are at least partially interpenetrated at the molecular level, characterised in that the plasticiser is at least one compound selected from the group consisting of:

a) polyols formed by from 1 to 20 repeating hydroxylated units each unit including from 2 to 6 carbon atoms, provided that when the polyol is formed by only one repeating unit it has at least 4 carbon atoms, with the exclusion of sorbitol,

b) ethers, thioethers, inorganic and organic esters, acetals and amino-derivatives of polyols formed by from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms with the exclusion of acetic esters of glycerine, triethyl citrate and tributyl citrate.

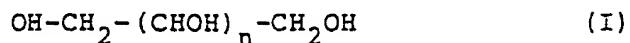
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c) polyol reaction products having from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms with chain extenders,

d) polyol oxidation products having from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms including at least one aldehydic or carboxylic functional group or mixtures thereof.

Compounds which have vapour pressures lower than that of glycerine at ambient temperature (25°C) and which are soluble in water are preferred.

The aliphatic polyols of type a) include compounds of the formula



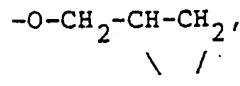
in which n is from 2 to 4, such as erythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol and allitol, and polyols which do not fall within the formula given above, such as trimethylolpropane, pentaerythritol, polyvinyl alcohol with from 3 to 20 repeating units and polyglycerol formed by from 2 to 10, preferably from 2 to 5, monomer units including mixtures of various oligomers.

The aliphatic polyol derivatives of paragraph b) preferably have structural formulae which can be obtained by the substitution of at least one alcoholic function of the polyol in question, which is preferably selected from those cited in the preceding paragraph including sorbitol, by a functional group selected from:

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- O-(CH₂)_n-H in which n = 1-18, preferably 1-4,
- O-CH=CH-R₁ in which R₁ = H, or -CH₃,
- O(-CH₂-CHR₁-O)_n-H in which R₁ = H, or CH₃ and n = 1-20,
- O-(CH₂)_n-Ar in which Ar is a simple, substituted or heterocyclic aromatic radical and n = 0-4,
- OCO-H,
- OCO-CR₁R₂R₃ in which the R₁, R₂, and R₃ groups are the same or different and are selected from H, Cl and F,
- OCO-(CH₂)_n-H in which n = 2-18, preferably 2-5,
- ONO₂,
- OPO₃²⁻M₂ in which M may be H, ammonium, an alkali metal, an alkaline earth or an organic cation, particularly trimethylammonium, pyridinium or picoline,
- SO₃-Ar in which Ar is benzene or toluene,
- OCO-CH(SO₃M)-COOM in which the Ms are the same or different and are selected from H, an alkali metal, an alkaline earth, ammonium or an organic cation, particularly pyridinium, picoline or methylammonium,
- OCO-B-COOM in which B is (CH₂)_n where n=1-6 or -CH=CH-, M may be H, an alkali metal, an alkaline earth, -(CH₂)_nH where n=1-6 or an aryl group,
- OCONH-R₁ in which R₁ may be -H or an aliphatic or aromatic radical,
- O-(CH₂)_n-COOM in which n=1-6 and M may be H or an alkali metal, an alkaline earth, ammonium, or an organic cation, particularly pyridinium, trimethylammonium or picoline,
- O-(CH₂)_n-COOR₁ in which n=1-6, R₁ = H(CH₂)_m- where m=1-6,
- NR₁R₂ in which R₁ and R₂ = H, CH₃-, CH₃CH₂-,
-CH₂-CH₂OH, or a salified amino group,
- O-(CH₂)_n-NR₁R₂ in which n=1-4, R₁ and R₂ = H, CH₃-,
CH₃CH₂-, or -CH₂-CH₂OH and in which the amino group

may be salified,



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$-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{NR}_1\text{R}_2$ in which R_1 and R_2 are the same or different and are selected from H, and $\text{H}(\text{CH}_2)_n$ where $n=1-6$, and in which the amino group may be salified,

$-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{R}_1^+\text{Cl}^-$ in which R_1^+ is trialkylammonium, pyridinium or picoline,

$-\text{O}-(\text{CH}_2)_n\text{R}_1\text{Cl}^-$ in which $n=1-6$ and R_1 is trialkylammonium, pyridinium or picoline,

$-\text{O}-(\text{CH}_2)_n-\text{CN}$ in which $n=1-6$,

$-\text{O}-(\text{CH}_2)_n-\text{CONH}_2$ in which $n=1-6$,

$-\text{O}-(\text{CH}_2)_m-\text{SO}_2-(\text{CH}_2)_n-\text{H}$ in which m and $n = 1-4$,

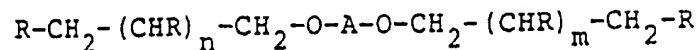
$-\text{SCSNH}_2^+$,

$-\text{O}-\text{SiX}_3$ and $-\text{O}-\text{SiO}_3$ in which X may be an aliphatic or an aromatic radical.

Mono- and di-ethers and mono- and di-esters of the polyols of formula (I) given above are particularly preferred and monoethoxylate, monopropoxylate and monoacetate derivates, particularly of sorbitol, are most preferred.

The compounds of paragraph c) result from the joining of two or more polyol molecules by means of chain extenders such as bicarboxylic acids, aldehydes and isocyanates, in particular.

Preferred are compounds of the formula:

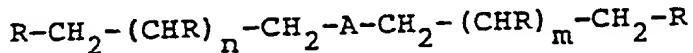


in which n and m have the same or different values from

1 to 6, the R groups are the same or different and are hydroxyl groups or have the meaning given above, and in which A is selected from the group consisting of

-CHR₁, R₁=H or H-(CH₂)_n - where n=1-5 (acetals),
-(CH₂)_n - where n=1-6,
-(CH₂-O-CH₂)_n in which n = 1-20,
-(CH₂CH₂-O)_n-CH₂CH₂- in which n=1-20,
-OC-(CH₂)_n-CO- in which n=0-6,
-OC-Ar-CO- in which Ar is an aromatic radical which is also heterocyclic,
-PO₂⁻,
-CONH-(CH₂)_nNHCO-,

and compounds of the formula:



in which n and m are the same or different and are whole numbers from 1 to 6, the R groups are the same or different and are hydroxyl groups or have the meaning given above and in which A is selected from the group consisting of -NH- and -NH-(CH₂-CH₂-NH)_n- in which n is a whole number from 1 to 6.

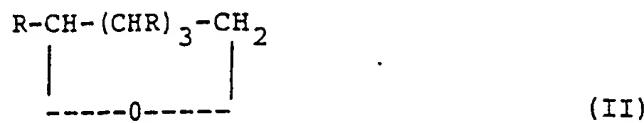
Of the compounds given above, compounds in which only one of the R groups is a group forming an ether or an ester are preferred.

The term "polyol" is intended to include mono- and polysaccharides with up to 20 monosaccharide units.

The following monosaccharides come into consideration in particular:

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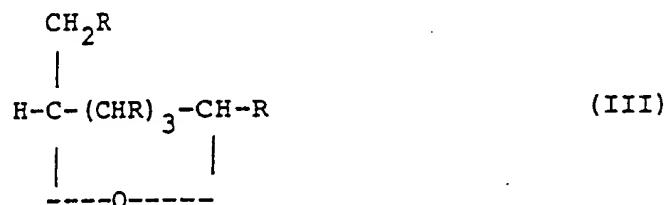
- pentoses and their derivatives of the formula:



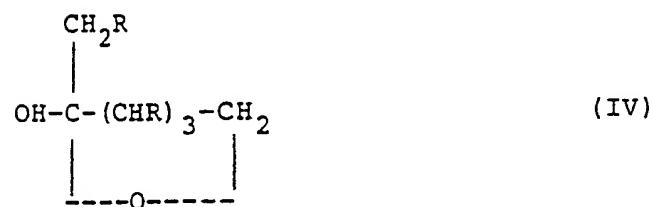
in which the R groups are the same or different and are hydroxyl groups or have the meaning given above.

Examples of such compounds are arabinose, lycose, ribose and xylose and, preferably, monoethers and monoesters thereof,

- aldohexoses and their derivatives of the formula:



and ketohexoses and their derivatives of the formula:



in which the R groups are the same or different and are hydroxyl groups or have the meaning given above.

Examples of these monosaccharides are glucose, fructose, mannose, allose, altrose, galactose, gulose, iodose, inositol, sorbose and talitol.

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of their etherified or esterified derivatives, monoethoxylate and monopropoxylate derivatives and monoesters, particularly of acetic acid, are preferred.

The polysaccharides include compounds having up to 20 repetitive units of formula (II), (III) or (IV) with molecular weights up to that of dextrin.

The R functional groups may be introduced into the basic polyol structure by known reactions, for example as described in Chapter 9 and in the literature cited in the publication "Polyvinyl alcohol" edited by C.A. Finch.

The oxidation products of the polyols of paragraph d) are obtained by the reaction of the polyols in question with periodic acid, hypochlorite or lead tetra-acetate.

The starch used in the polymeric compositions is preferably a native starch, particularly maize starch, but the term starch is intended also to include physically and chemically modified starches such as those cited in the same Applicant's applications Nos. EP-A-413798 and EP-A-400532.

For the synthetic polymeric component, the hydrophilic or essentially hydrophobic polymers described in the literature may be used in the starchy compositions. Of these, ethylene copolymers containing more than 50% by weight of ethylene and having melting points between 80 and 130°C, such as ethylene-acrylic acid, ethylene-vinyl alcohol, ethylene-vinyl acetate and mixtures thereof are considered in particular.

However, particularly preferred are polyvinyl alcohols and

ethylene-vinyl alcohol copolymers with ethylene contents of less than 40% by weight with various degrees of hydrolysis, produced by the hydrolysis of the corresponding polyvinyl acetate or ethylene vinyl acetate respectively. The degree of hydrolysis of the ethylene-vinyl alcohol copolymer is preferably between 100% and 50%.

The alcoholic units of the polymers mentioned above may be partly or wholly modified to produce:

1) ethers resulting from reaction with:

- ethylene oxide,
- ethylene oxide substituted by alkyl radicals up to C_{20} or by aromatic radicals,
- acrylonitrile (Ce^{2+} initiator),
- acrylamide,
- arylalkyl halides,
- chloroacetic acid,
- methylchloromethyl ether,
- silanes

2) inorganic and organic esters such as sulphates, nitrates, phosphates, arsenates, xanthates, carbamates, urethanes, borates, titanates,

3) organic esters resulting from reactions with aliphatic or aromatic acids, chloroacyls, particularly of fatty acids or anhydrides,

4) acetals and ketals produced by reaction with:

- aliphatic aldehydes with up to 22 carbon atoms,
- unsaturated aliphatic aldehydes with up to 22 carbon

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- atoms,
- chloroacetaldehyde,
- glyoxal,
- aromatic aldehydes,
- cyclic aliphatic aldehydes,
- aliphatic ketones,
- arylalkyl ketones,
- alkylcycloalkyl ketones.

The reactions to produce the organic and inorganic esters and the acetals given above can easily be achieved as described in Chapter 9 and the literature cited in the publication "Polyvinyl alcohol" edited by C.A. Finch.

It is also possible to use polyvinyl alcohol and ethylene-vinyl alcohol multifunctional polymers (with ethylene contents of up to 40% by weight and degrees of hydrolysis of the acetate of between 100 and 50%) in which up to 50% of the ethylene may be substituted by co-monomers selected from the group consisting of:

propylene, isobutene, styrene, vinyl chloride, 1,1-dichloroethene, vinyl ethers of the formula $\text{CH}_2 = \text{CR-OR}'$ in which R is hydrogen or a methyl group and R' is an alkyl group with from 1 to 18 carbon atoms, a cycloalkyl group or a polyether, acrylonitrile, methacrylonitrile, vinyl ketones of the formula $\text{CH}_2 = \text{CR-CO-CH}_2-\text{R}'$ in which R is hydrogen or a methyl group and R' is hydrogen or a C_1-C_6 alkyl group, acrylic or methacrylic acid or their esters of the formula $\text{CH}_2 = \text{CR-COOR}'$ in which R is hydrogen or a methyl group and R' is hydrogen or a C_1-C_6 alkyl group and the alkali metal or alkaline earth salts of these acids, vinyl derivatives of the formula $\text{CH}_2 = \text{CR-OCOR}'$

in which R is hydrogen or a methyl group and R' is hydrogen, a methyl group, a methyl group mono-, bi- or tri-substituted with chloro or fluoro groups or C₂-C₆ alkyl groups, vinylcarbamates of the formula CH₂ = CR-CONR'R'', in which R is hydrogen or a methyl group and R' and R'' are the same or different and are hydrogen or C₁-C₃ alkyl groups, maleic anhydride, fumaric anhydride, vinylpyrrolidone, vinylpyridine, or 1-vinylimidazole.

The copolymerisation is achieved with the use of radical initiators such as hydrogen peroxide, peroxy sulphates and benzoyl peroxides, as described in the chapter "Polymerisation processes of vinyl esters" and the literature cited on pages 406 et. seq. of Volume 17 of the "Encyclopedia of Polymer Science and Engineering".

The aforementioned plasticisers may also be used in compositions including starch, a first synthetic component selected from ethylene-vinyl alcohol copolymer, possibly modified polyvinyl alcohol and mixtures thereof and a further synthetic component comprising one or more polymers such as hydrophobic polymers of polyethylene or of its vinyl copolymers such as those cited above, or aliphatic polyesters (e.g. polyvinyl acetate, polycaprolactone, polyhydroxybutyrate (PHP) and polyhydroxybutyrate valerate (PHBV), polylactic acid, polyethylene and polybutylene adipates or sebacates), polyethers (e.g. polyoxymethylene, polyoxyethylene, polyoxypropylene, polyphenylene oxide), polyamides (nylon 6, nylon 12, etc.) polyacrylonitrile, polyurethanes, polyester/polyurethane copolymers, polyester/polyamide copolymers, polyglycolide or hydrophilic polymers such as: polyvinyl pyrrolidone, polyoxazoline, cellulose acetates and nitrates, regenerated cellulose, alkyl cellulose, carboxymethyl cellulose, casein-type proteins and salts thereof, natural gums such as gum arabic, algin

and alginates, chitin and chitosan.

The relative proportions of starch and synthetic copolymer in the composition may vary within wide limits and is generally between 1:99 and 99:1 (anhydrous starch / synthetic polymer), preferably between 1:9 and 9:1.

As far as the biodegradability properties of the polymeric compositions produced are concerned, the compositions with high starch contents and particularly compositions in which the anhydrous starch content is from 20 to 80% of the total quantity of anhydrous starch and synthetic polymer are preferred.

When a blend of synthetic polymers is used, including the above mentioned first and second hydrophobic or hydrophilic synthetic component, the weight ratio of said component is preferably between 1:6 and 6:1.

The concentration of the plasticiser may vary within wide limits in dependence of the mechanical properties to be obtained in the articles produced with the use of the polymeric composition. The concentration of the plasticiser is preferably from 1 to 50% and most preferably from 5 to 40% of the total composition by weight.

The polymeric material may also include agents which can destroy hydrogen bonds, such as urea and alkali-metal or alkaline-earth hydroxides which are added to the starch and copolymer mixture in quantities of between 0.5 and 20% of the weight of the entire composition.

The polymeric material may also include cross-linking agents, such as aldehydes, ketones and glyoxals, process coadjuvants and release and lubricating agents normally incorporated in compositions for moulding or extrusion, such as fatty acids, fatty-acid esters.

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higher alcohols, polythene waxes, fungicides, flame-proofing agents, herbicides, antioxidants, fertilisers, opacifiers and stabilisers.

The polymeric composition is preferably prepared by the mixing of the components cited above in an extruder heated to a temperature generally between 100 and 220°C. The composition supplied to the extruder includes water due to the intrinsic water content of the starch used (9-15% by weight) and water may be added as appropriate.

In order to produce articles with suitable mechanical properties as a result of the moulding or extrusion of the polymeric composition, the water content of the total composition is preferably reduced by intermediate degassing during the extrusion to a water content which varies according to the transformation technology and the degree of rigidity required of the final material.

The pressures to which the mixture is subjected during the heat treatment are typical for extrusion in single- and double-screw extruders. Although the process is preferably carried out in an extruder, the starch, synthetic polymer and plasticiser may be mixed by any device which ensures conditions of temperature and shearing stress suitable to render the starch and the polymer used compatible from a rheological point of view.

If synthetic polymers with high melting points, such as, for example, polyvinyl alcohol and ethylene-vinyl alcohol copolymer with ethylene contents no greater than 40% by weight are used, in particular, the plasticisers described also perform an important

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function in the process which leads to the formation of a composition with an (at least partially) interpenetrated structure. The melting points of these polymers (160-200°C) are so high that complete interpenetration with the starch molecules is impossible; the addition of plasticisers common to the starchy and polymeric components lowers the melting points of the synthetic polymers and at the same time changes their rheological behaviour.

Solely for this function, and with the synthetic polymers cited in the present description which have melting points of the order of 160-200°C, conventional plasticisers such as ethylene glycol, propylene glycol, sorbitol and glycerine can also be used either alone or mixed with the plasticisers described.

The preferred method of preparing the compositions of the invention includes the following steps:

- swelling the starch and synthetic polymer by means of the plasticiser and possibly water at a temperature between 80 and 180°C with a dynamic change in their melting points and rheological behaviour; this effect can be achieved, for example, during a first stage of the transportation of the components in an extruder, for periods of the order of 2 to 50 seconds,
- subjecting the mixture to shearing conditions corresponding to similar viscosity values of the two components so as to cause the interpenetration of the molecules of the two components,
- degassing the mixture freely, under controlled pressure or under vacuum to produce a melt at a

temperature of 140-180°C with a liquid content such that bubbles are not created at atmospheric pressure, that is, for example, at the output of the extruder,
- cooling the finished product in a water bath or in air.

The whole method requires a pressure of between 0.5 and 10 MPa, preferably between 1 and 5 MPa.

As stated, the thermoplastic composition is preferably prepared by mixing the components cited directly; the starch may, however, also be treated beforehand in the presence of a plasticiser, possibly with added water, at a temperature of from 100 and 220° to produce a thermoplastic starch. This starch can be mixed with the synthetic polymer and a further quantity of plasticiser in a second step. For polyvinyl alcohol and ethylene-vinyl alcohol copolymer, a portion of the total quantity of plasticiser is added at the start of the mixing of the pretreated starch and the synthetic polymer since the plasticiser itself has to be available to modify the melting point and rheological behaviour of the polymer in order to make it compatible with the starch.

When a blend including a first synthetic component and a second synthetic component, as previously defined, is used, the process for preparing the compositions according to the invention may also be carried out by blending the first synthetic component with starch and plasticiser to obtain pellets and then blending such pellets with the second synthetic component in a subsequent extrusion step.

Example 1 (comparative):

37 parts of Globe 3401 starch (11% by weight of water), 37 parts of ethylene vinyl alcohol with an ethylene content

of 42% in moles and a degree of hydrolysis of the acetate groups of 99.5%, 3 parts of ethylene-acrylic acid copolymer with 20% of acrylic acid and a melt flow of 2 (at 125°C and a 0.325 kg load), 0.3 parts of Armid E, 5 parts of urea, 15 parts of glycerine, and 2.7 parts of water were mixed in a single-screw OMC extruder with a diameter d of 20 mm and an L/d of 30, operating with the following temperature profile: 90-180-150-140°C and having an intermediate degassing section. The extruded and granulated product which had a water content of 3.2% by weight was then moulded in an injection press to form plates with dimensions of 70 x 70 x 1 mm which were then inserted in a climatic cell programmed to carry out cycles from 20°C and 30% relative humidity to 30°C and 80% relative humidity over 6 hours for a total of 20 cycles.

After this treatment, the plates were oily.

Example 2:

A composition corresponding to that of the comparative Example 1 in which the glycerine was replaced by a polyglycerol formed by condensation and having an average glycerine content of 4 moles.

The plates obtained and treated as described in Example 1 showed neither significant bleeding nor loss of plasticiser during the aging period.

Example 3 (comparative):

A composition identical to that of Example 1 was used but with the use of sorbitol instead of glycerine.

At the end of the heating cycles, the plates had an aesthetically-unacceptable white dusty surface appearance.

Examples 4-12:

Compositions identical to those of Example 1 were used with the glycerine replaced as indicated below.

In all cases the appearance of the plates after the heating cycles was aesthetically good since they did not appear oily and were not receptive to fingerprints neither did the plates show any loss of plasticiser over the period.

Example No.	Plasticiser
4	Sorbitol acetate
5	Sorbitol diacetate
6	Sorbitol monoethoxylate
7	Sorbitol diethoxylate
8	Sorbitol dipropoxylate
9	Sorbitol hexapropoxylate
10	Aminosorbitol
11	Trihydroxymethylamino-methane
12	Glucose/PEG (20 moles PEG) product of the reaction of glucose with ethylene oxide.

Some of the compositions given above were filmed by blowing.

The mechanical characteristics of the films produced were generally good and in some cases better than the formulations with glycerine.

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Example	Load MPa	Extension %	Modulus MPa	Energy KJ/m ²
1	15	330	180	1650
3	14	250	155	1400
4	11	360	165	1700
5	10	180	340	1250
6	18	340	280	2150
7	13	310	160	1650
8	14	310	170	1540
9	10	35	390	650

Other plasticisers include:

- trimethylolpropane monoethoxylate,
- mannitol monoacetate,
- mannitol monoethoxylate,
- butyl glucoside,
- alpha-methyl glucoside,
- glucose monoethoxylate,
- the sodium salt of carboxymethylsorbitol,
- polyglycerol monoethoxylate (degree of polymerisation 3.9).

In the compositions according to the invention, and in the articles formed from these compositions, starch and the synthetic polymer form a structure which is at least partly interpenetrated at the molecular level. Particularly in the case of compositions in which the synthetic polymeric component comprises ethylene-vinyl alcohol polymer with the concentrations of starch and polymer in a ratio of from 1:4 to 4:1, the composition is considered to have an at least partly interpenetrated structure when one or more of the

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following phenomena occur:

- the starchy phase cannot be separated from the ethylene vinyl alcohol phase (EVOH) by making use of the solubility of the starch. This phenomenon can be observed not only in cold water but also in water at 100°C. In this case, the sample tends to break up but the separated particles retain the same proportions of EVOH and starch (FTIR method),
- a microstructure observed by TEM which may exhibit a complete absence of phases or the presence of phases with dimensions smaller than 0.3 microns; the phases are mixed with each other without clear outlines,
- the presence in the tg delta spectrum, upon dynamic-mechanical analysis, of a single beta transition linked to the mobility of the -OH groups of both the components with a modification of the peak from that of starch,
- mechanical properties close to those of PE at a T of 23°C and 50% humidity. Extensibility between 80 and 600% and breaking energy comparable with those of PE are achieved. These characteristics are far removed from those of the two starting products.

Moreover, phase separation would tend to reduce the extensibility and breaking energy.

This whole set of characteristics can be explained as resulting from "entanglements" of starch and EVOH chains which are made stronger than the amylopectin "branches", and the stabilisation of the structure by hydrogen bonds. This explanation is in no way binding

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with reference to the scope of the protection of the invention.

Formed articles, films, sheets and fibres produced from the polymeric compositions by injection moulding, extrusion, blow-extrusion, thermoforming and similar conventional methods for thermoplastics materials fall within the scope of the invention.

Specific applications comprise: films for nappies, mulch, packaging in general, films for protective coatings or films coextruded with biodegradable and non-biodegradable polymers,

- injection mouldings for syringe parts, tampon applicators, plant pots, etc.,
- thermoformed trays, bowls, blister packs,
- combinations with aluminium, paper or other polymers,
- extrusions such as cotton-wool sticks, sheets for thermoforming, folders for stationery, etc.,
- products expanded solely by water or by gases such as CO_2 , applications in the packaging and hamburger-tray sectors and the like,
- fibres for wadding, non-woven fabrics and melt blow,
- bottles and containers produced by blow moulding.

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CLAIMS

1. A thermoplastic polymeric composition including starch, at least one synthetic thermoplastic polymer and a plasticiser and in which the starch and the polymer form a structure in which they are at least partially interpenetrated at the molecular level, characterised in that the plasticiser is at least one compound selected from the group consisting of:

- a) polyols formed by from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms, provided that when the polyol is formed by only one repeating unit it has at least 4 carbon atoms, with the exclusion of sorbitol,
- b) ethers, thioethers, inorganic and organic esters, acetals and amino-derivatives of polyols formed by from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms with the exclusion of acetic esters of glycerine, triethyl citrate and tributyl citrate,
- c) polyol reaction products having from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms with chain extenders,
- d) polyol oxidation products having from 1 to 20 repeating hydroxylated units each including from 2 to 6 carbon atoms including at least one aldehydic or carboxylic functional group or mixtures thereof.

2. A polymeric composition according to Claim 1 in which the plasticiser is selected from the group consisting of polyglycerol having from 2 to 10

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monomeric units, polyvinyl alcohol having from 3 to 20 monomeric units, erythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol, allitol, trimethylolpropane and pentaerythritol.

3. A composition according to Claim 1 in which the plasticiser is a monoethoxylate, monopropoxylate or monoacetate derivative of sorbitol or of a polyol mentioned in Claim 2.

4. A polymeric composition according to Claim 1, in which the plasticiser is a derivative of an aliphatic polyol having from 3 to 6 carbon atoms in which one alcoholic function is replaced by a functional group R selected from the group consisting of:

- O-(CH₂)_n-H in which n = 1-18, preferably 1-4,
- O-CH=CH-R₁ in which R₁ = H, or -CH₃,
- O(-CH₂-CHR₁-O)_n-H in which R₁ = H, or CH₃ and n = 1-20,
- O-(CH₂)_n-Ar in which Ar is a simple, substituted or heterocyclic aromatic radical and n = 0-4,
- OCO-H,
- OCO-CR₁R₂R₃ in which the R₁, R₂, and R₃ groups are the same or different and are selected from H, Cl and F,
- OCO-(CH₂)_n-H in which n = 2-18, preferably 2-5,
- ONO₂,
- OPO₃^{M₂} in which M may be H, ammonium, an alkali metal, an alkaline earth or an organic cation, particularly trimethylammonium, pyridinium or picoline,
- SO₃-Ar in which Ar is benzene or toluene,
- OCO-CH(SO₃^{M₂})-COOM in which the Ms are the same or different and are selected from H, an alkali metal, an alkaline earth, ammonium, or an organic cation, particularly pyridinium, picoline or

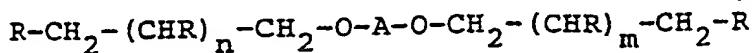
methylammonium,

- OCO-B-COOM in which B is $(\text{CH}_2)_n$ where n=1-6 or
-CH=CH-, M may be H, an alkali metal, an alkaline earth, $-(\text{CH}_2)_n\text{H}$ where n=1-6, or an aryl group,
- OCONH-R₁ in which R₁ may be -H or an aliphatic or aromatic radical,
- O-(CH₂)_n-COOM in which n=1-6 and M may be H, an alkali metal, an alkaline earth, ammonium, or an organic cation, particularly pyridinium, trimethylammonium or picoline,
- O-(CH₂)_{2n}-COOR₁ in which n=1-6, R₁ = H(CH₂)_m- where m=1-6,
- NR₁R₂ in which R₁ and R₂ = H, CH₃-, CH₃CH₂-,
-CH₂-CH₂OH, or a salified amino group,
- O-(CH₂)_n-NR₁R₂ in which n=1-4, R₁ and R₂ = H, CH₃-, CH₃CH₂-, or -CH₂-CH₂OH, and in which the amino group may be salified,
- O-CH₂-CH-CH₂,
 \ /
 O
- O-CH₂-CHOH-CH₂-NR₁R₂ in which R₁ and R₂ are the same or different and are selected from H, H(CH₂)_n where n=1-6, and in which the amino group may be salified,
- O-CH₂-CHOH-CH₂-R₁⁺Cl⁻ in which R₁⁺ is trialkylammonium, pyridinium or picoline,
- O-(CH₂)_nR₁⁺Cl⁻ in which n=1-6 and R₁⁺ is trialkylammonium, pyridium or picoline,
- O-(CH₂)_n-CN in which n=1-6,
- O-(CH₂)_n-CONH₂ in which n=1-6,
- O-(CH₂)_m-SO₂-(CH₂)_n-H in which m and n = 1-4,
- SCSNH₂,
- O-SiX₃ and -O-SiOX₃ in which X may be an aliphatic or an aromatic radical.

5. A composition according to Claim 1 in which the

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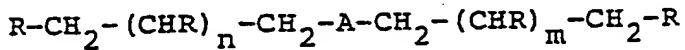
plasticiser is a compound of the formula:



in which n and m have the same or different values from 1 to 6, the R groups are the same or different and are hydroxyl groups or have the meaning attributed to R in Claim 4, and in which A is selected from the group consisting of:

- CHR_1 $R_1=H$ or $H-(CH_2)_n-$ where $n=1-5$ (acetals),
- $(CH_2)_n-$ where $n=1-6$,
- $(CH_2-O-CH_2)_n$ in which $n = 1-20$,
- $(CH_2-CH_2-O)_n-CH_2-CH_2-$ in which $n=1-20$,
- $OC-(CH_2)_n-CO-$ in which $n=0-6$,
- $OC-Ar-CO-$ in which Ar is an aromatic radical which is also heterocyclic,
- PO_2^- ,
- $CONH-(CH_2)_n-NHCO-$.

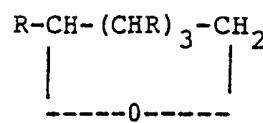
6. A composition according to Claim 1, in which the plasticiser is a compound of the formula:



in which n and m are the same or different and are whole numbers from 1 to 6, the R groups are the same or different and are hydroxyl groups or have the meaning given in Claim 4 and in which A is selected from the group consisting of - $NH-$ and - $NH-(CH_2-CH_2-NH)_n-$ in which n is a whole number from 1 to 6.

7. A composition according to Claim 1 in which the plasticiser is a compound of the formula:

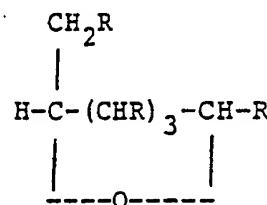
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(II)

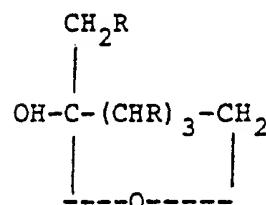
in which the R groups are the same or different and are hydroxyl groups or have the meaning attributed to R in Claim 4.

8. A composition according to Claim 1, in which the plasticiser is an aldohexose or a derivative thereof of the formula:



(III)

or a ketohexose or a derivative thereof of the formula:



(IV)

in which the R groups are the same or different and are hydroxyl groups or have the meanings given in Claim 4.

9. A composition according to any one of Claims 7 or 8 in which the plasticiser is a compound of formula (II), (III) or (IV) in which one of the R groups has the meaning given in Claim 4 and the rest of the R groups are hydroxyl groups.

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10. A composition according to Claim 1, in which the plasticiser is selected from the group consisting of arabinose, lycose, xylose, glycose, fructose, mannose, allose, altrose, galactose, gulose, iodose, inositol, sorbose, talitol and monoethoxylate, monopropoxylate and monoacetate derivatives thereof.

11. A composition according to Claim 1 in which the plasticiser d) is the product of oxidation by an oxidising reagent selected from periodic acid, hypochlorite and lead tetraacetate.

12. A composition according to any one of the preceding claims, in which the weight of the plasticiser is from 1 to 50%, preferably from 5 to 40%, of the weight of the composition.

13. A composition according to any one of the preceding claims, in which the thermoplastic polymer is selected from the group consisting of polyvinyl alcohol, ethylene-acrylic acid, ethylene-vinyl acetate, ethylene-vinyl alcohol, modified ethylene-vinyl alcohol, modified polyvinyl alcohol and mixtures thereof.

14. A composition according to Claim 13 including a polymer of ethylene vinyl alcohol produced by the hydrolysis of the corresponding ethylene vinyl acetate with a degree of hydrolysis of the acetate groups of from 50 to 100% and an ethylene content less than 40% by weight.

15. A composition according to Claim 13 including a polymer of ethylene vinyl alcohol or polyvinyl alcohol having alcoholic functional groups which are at least partly etherified by reaction with a compound selected

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from the group consisting of ethylene oxide either unsubstituted or substituted by C₁-C₂₀ alkyl radicals or aromatic radicals, acrylonitrile, acrylamide, arylalkyl halides, chloroacetic acid, methylchloromethylether and silanes.

16. A composition according to Claim 13 including a polymer of ethylene vinyl alcohol or polyvinyl alcohol including esterified alcoholic functional groups selected from the group consisting of sulphates, nitrates, phosphates, arsenates, xanthates, borates, titanates, urethanes and carbamates.

17. A composition according to Claim 13 including a polymer of ethylene vinyl alcohol or polyvinyl alcohol including alcoholic functional groups esterified by reaction with aliphatic or aromatic acids, chloroacyls or anhydrides.

18. A composition according to Claim 13 including a polymer of ethylene vinyl alcohol or polyvinyl alcohol including acetal functional groups produced by reaction with compounds selected from the group consisting of saturated and unsaturated aliphatic aldehydes having up to 22 carbon atoms, aromatic aldehydes, cycloaliphatic aldehydes, chloroacetaldehyde, glyoxal, aliphatic ketones, alkylcycloalkyl ketones and arylalkyl ketones.

19. A composition according to Claim 13 including a multifunctional copolymer of ethylene-vinyl alcohol with an ethylene content up to 40% by weight and a degree of hydrolysis of the acetate between 100 and 50% in which up to 50% of the ethylene may be replaced by co-monomers selected from the group consisting of:

propylene, isobutene, styrene, vinyl chloride, 1,1-dichloroethene, vinyl ethers of the formula $\text{CH}_2 = \text{CR-OR}'$ in which R is hydrogen or a methyl group and R' is an alkyl group with from 1 to 18 carbon atoms, a cycloalkyl group or a polyether, acrylonitrile, methacrylonitrile, vinyl ketones of the formula $\text{CH}_2 = \text{CR-CO-CH}_2-\text{R}'$ in which R is hydrogen or a methyl group and R' is hydrogen or a C_1-C_6 alkyl group, acrylic or methacrylic acid or their esters of the formula $\text{CH}_2 = \text{CR-COOR}'$ in which R is hydrogen or a methyl group and R' is hydrogen or a C_1-C_6 alkyl group and the alkali metal or alkaline earth salts of these acids, vinyl derivatives of the formula $\text{CH}_2 = \text{CR-OCOR}'$ in which R is hydrogen or a methyl group and R' is hydrogen, a methyl group, a methyl group mono- bi- or tri-substituted by chloro- or fluoro groups or C_2-C_6 alkyl groups, vinylcarbamates of the formula $\text{CH}_2 = \text{CR-CONR'R''}$, in which R is hydrogen or a methyl group and R' and R'' are the same or different and are hydrogen or C_1-C_3 alkyl groups, maleic anhydride, fumaric anhydride, vinylpyrrolidone, vinylpyridine, or 1-vinylimidazole.

20. A composition according to any one of Claims 13 to 19 including starch, ethylene-vinyl alcohol copolymer and/or polyvinyl alcohol, possibly modified, and a polymer selected from the hydrophobic polymers of polyethylene or its vinyl copolymers, aliphatic polyesters, particularly polyvinyl acetate, polycaprolactone, PHB, PHBV, polylactic acid, polyethylene and polybutylene adipates or sebacates, polyethers, particularly polyoxymethylene, polyoxyethylene, polyoxypropylene, polyphenylene oxide, polyamides, polyacrylonitrile, polyurethanes, polyester/polyurethane copolymers, polyesters/polyamide

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copolymers, polyglycolide and hydrophilic polymers such as: polyvinyl pyrrolidone, polyoxazoline, cellulose acetates and nitrates, regenerated cellulose, alkyl cellulose, carboxymethyl cellulose, casein-type proteins and salts thereof, natural gums, chitin and chitosan.

21. Articles formed from a polymeric composition according to any one of the preceding claims.

22. The use of the compounds cited in Claims 1 to 11 as plasticisers in starchy compositions.

23. A method of preparing a polymeric composition according to any one of Claims 1 to 20, characterised in that it includes the step of mixing starch, a synthetic polymer, a plasticiser and possibly water under temperature and pressure conditions of between 100 and 220°C and from 0.5 to 100 MPa.

24. A method of preparing a polymeric composition according to any one of Claims 1 to 20 including the steps of:

a) mixing starch, a synthetic polymer and a plasticiser at a temperature between 80 and 180°C for a period such that the plasticiser causes the bulking of the starch and the polymer,

b) subjecting the mixture thus obtained to shearing conditions corresponding to similar viscosity values of the starchy and synthetic components so as to cause the interpenetration of the two components at the molecular level.

30.
25. A method according to Claim 24 in which the mixture in a) includes water and including a step for degassing the mixture obtained in b) at a temperature from 140 to 180°C so as to obtain a molten mixture with a liquid content such as to avoid the formation of bubbles at atmospheric pressure.

26. A method according to Claim 24 in which the mixing periods in step a) are from 2 to 50 seconds.

27. A method according to Claim 24, in which the mixture is kept under a pressure of from 0.5 to 10 MPa during steps a) and b).

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/00320

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁴

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵ : C 08 L 3/02, C 08 K 5/07

II. FIELDS SEARCHED

Minimum Documentation Searched⁶

Classification System	Classification Symbols
IPC ⁵	C 08 L 3/00, C 08 K 5/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁶III. DOCUMENTS CONSIDERED TO BE RELEVANT⁷

Category ⁸	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹¹	Relevant to Claim No. ¹¹
A	EP, A2, 0 327 505 (WARNER-LAMBERT) 09 August 1989 (09.08.89), see claims 1, 20, 23, 24 (cited in the application). --	1, 21, 24
A	EP, A1, 0 400 532 (BUTTERFLY) 05 December 1990 (05.12.90), see claims 1, 9, 13, 14, 16 (cited in the application). --	1, 21, 24
A	EP, A2, 0 404 728 (WARNER-LAMBERT) 27 December 1990 (27.12.90), see claim 1 (cited in the application). --	1
A	WO, A1, 90/10 671 (BUTTERFLY) 20 September 1990 (20.09.90), see claim 1	1, 21

⁴ Special categories of cited documents:¹⁰

- ^{"A"} document defining the general state of the art which is not considered to be of particular relevance
- ^{"E"} earlier document but published on or after the International filing date
- ^{"L"} document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- ^{"O"} document referring to an oral disclosure, use, exhibition or other means
- ^{"P"} document published prior to the International filing date but later than the priority date claimed

⁷ later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention⁸ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step⁹ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁰ document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

04 April 1992

Date of Mailing of this International Search Report

08 MAY 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

MISS T. TAZELAAR

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	(cited in the application). -- WO, A1, 88/06 609 (AMROTEX) 07 September 1988 (07.09.88), see claims 1,4. --	1
A	CHEMICAL ABSTRACTS, vol. 86, no. 26, issued 1977, June 27, (Columbus, Ohio, USA), E.B. BAGLEY et al. "Graft copolymers of poly- saccharides with thermo- plastic polymers. A new type of filled plastic.", see page 18, column 1, the abstract-no. 190 711d, Polym. Eng. Sci. 1977, 17(5), 311-16 (Eng). -----	1

ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

ANNEXE

au rapp de recherche internationale relatif à la demande de brevet international n°

PCT/EP 92/00320 SAE 56128

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unter-richtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visé ci-dessus. Les renseignements fournis sont donnés à titre indica-tif et n'engagent pas la responsabilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2 327505	09-08-89	AU A1 28876/89 AU B2 617411 BR A 8900350 CN A 1036215 DK A0 367/89 DK A1 367/89 EP A3 327505 FI A0 890406 FI A1 890406 GB A0 8802313 GB A1 2214918 HU A2 58776 IL A0 89096 JP A2 2014228 NO A0 890361 NO A1 890361 NZ A 227762 PL A1 277424 PT A 89556 US A 5095054 ZA A 8900692 AU A1 59010/90 BR A 9003381 CA AA 2021118 CN A 1048862 EP A2 409789 EP A3 409789 FI A0 903554 HU A0 904215 HU A2 58777 IL A0 95079 JP A2 3103453 NO A0 903142 NO A1 903142 NZ A 234495 PT A 94706 ZA A 9005522 AU A1 58966/90 BR A 9003379 CA AA 2020893 CN A 1048863 EP A2 409783 EP A3 409783 FI A0 903501 HU A0 904170 HU A2 54399 IL A0 95043 JP A2 3095239 NO A0 903090 NO A1 903090 NZ A 234456 PT A 94659 ZA A 9005433 AU A1 58965/90 BR A 9003322 CA AA 2020894 CN A 1048864 EP A2 409782 EP A3 409782 FI A0 903500 HU A0 904171 HU A2 54400 IL A0 95042 JP A2 3056543	03-08-89 28-11-91 19-09-89 11-10-89 27-01-89 04-08-89 10-10-90 27-01-89 04-08-89 02-03-88 13-09-89 30-03-92 15-08-89 18-01-90 27-01-89 04-08-89 28-08-90 04-09-89 29-09-89 10-03-92 27-12-89 24-01-91 27-08-91 21-01-91 30-01-91 23-01-91 14-08-91 13-07-90 28-12-90 30-03-92 10-06-91 30-04-91 13-07-90 21-01-91 27-08-91 20-03-91 29-05-91 24-01-91 27-08-91 19-01-91 30-01-91 27-01-91 17-07-91 11-07-90 28-12-90 28-02-91 10-06-91 19-04-91 11-07-90 21-01-91 27-08-91 20-03-91 29-05-91 24-01-91 27-08-91 19-01-91 30-01-91 27-01-91 19-01-91 24-07-91 11-07-90 28-12-90 28-02-91 10-06-91 12-03-91

NO	A	903089	21-01-91
NZ	A	234455	27-08-91
		94658	-03-91
PT	A	9005435	29-05-91
AU	A1	58687/90	27-01-91
BR	A	9003216	27-08-91
CA	AA	2020404	12-01-91
EP	A2	408502	16-01-91
EP	A3	408502	12-06-91
FI	AO	903379	04-07-90
HU	AO	904093	28-12-90
HU	A2	54397	28-02-91
IL	AO	94965	10-06-91
JP	A2	3070752	26-03-91
NO	AO	902991	04-07-90
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NZ	A	234363	27-08-91
PT	A	94593	20-03-91
ZA	A	9005240	29-05-91
AU	A1	58688/90	17-01-91
BR	A	9003217	27-08-91
CA	AA	2020403	12-01-91
CN	A	1048712	23-01-91
EP	A2	408501	16-01-91
EP	A3	408501	08-05-91
FI	AO	903378	04-07-90
HU	AO	904092	28-12-90
HU	A2	54396	28-02-91
IL	AO	94964	10-06-91
JP	A2	3074445	29-03-91
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NZ	A	234362	27-08-91
PT	A	94592	20-03-91
ZA	A	9005242	29-05-91
AU	A1	58064/90	10-01-91
BR	A	9003200	27-08-91
CA	AA	2020150	07-01-91
CN	A	1048549	16-01-91
EP	A2	407350	09-01-91
EP	A3	407350	05-06-91
FI	AO	903315	29-06-90
HU	AO	904041	28-12-90
HU	A2	55813	28-06-91
IL	AO	94647	15-04-91
JP	A2	3074444	29-03-91
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NZ	A	234315	27-08-91
NA	A	9005126	29-05-91
AU	A1	59064/90	24-01-91
BR	A	9003344	27-08-91
CA	AA	2020895	19-01-91
CN	A	1048860	30-01-91
EP	A2	409781	23-01-91
EP	A3	409781	31-07-91
FI	AO	903499	11-07-90
HU	AO	904168	28-12-90
HU	A2	54398	28-02-91
IL	AO	95041	10-06-91
JP	A2	3074446	29-03-91
NO	AO	903087	11-07-90
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NZ	A	234454	27-08-91
PT	A	94657	20-03-91
ZA	A	9005434	29-05-91
AU	A1	57500/90	03-01-91
BR	A	9002853	20-08-91
CA	AA	2019084	22-12-90
CN	A	1048551	16-01-91
EP	A2	404728	27-12-90
EP	A3	404728	05-06-91
FI	AO	903028	15-06-90
HU	AO	903877	28-11-90
HU	A2	54393	28-02-91
IL	AO	94589	15-04-91
JP	A2	3079646	04-04-91
NO	AO	902677	15-06-90
NO	A	902677	27-12-90
NZ	A	234091	27-08-91
ZA	A	9004680	26-06-91
AU	A1	57501/90	03-01-91
BR	A	9002852	20-08-91
CA	AA	2019085	22-12-90
CN	A	1048550	16-01-91
EP	A2	404727	27-12-90
EP	A3	404727	22-05-91
FI	AO	903027	15-06-90

HU	A2	54394	28-04-91
IL	AO	94588	15-04-91
JP	A2	3143934	-06-91
NO	AO	902676	15-06-90
NO	A	902676	27-12-90
NZ	A	234018	27-08-91
ZA	A	9004670	29-05-91
AU	A1	57034/90	20-12-90
BR	A	9002792	20-08-91
CA	AA	2018785	19-12-90
CN	A	1048552	16-01-91
EP	A2	404723	27-12-90
EP	A3	404723	22-05-91
FI	AO	902931	12-06-90
HU	AO	903817	28-11-90
HU	A2	54392	28-02-91
IL	AO	94587	15-04-91
JP	A2	3079645	04-04-91
NO	AO	902602	12-06-90
NO	A	902602	20-12-90
NZ	A	234018	27-08-91
ZA	A	9004540	29-05-91
AU	A1	59009/90	24-01-91
BR	A	9003380	27-08-91
CA	AA	2021119	21-01-91
CN	A	1048861	30-01-91
EP	A2	409788	23-01-91
EP	A3	409788	07-08-91
FI	AO	903555	13-07-90
HU	AO	904212	28-12-90
HU	A2	57809	30-12-91
IL	AO	95080	10-06-91
JP	A2	3070753	26-03-91
NO	AO	903143	15-07-90
NO	A	903143	21-01-91
NZ	A	234496	27-08-91
PT	A	94707	20-03-91
ZA	A	9005523	29-05-91

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